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(54) Additives for controlling or modifying thixotropic properties

(57) An organoclay such as a Bentonite treated with a quaternary ammonium compound for use as an additive in controlling the thixotropic properties of drilling muds is modified by the addition of a minor proportion of salt of a long chain amine and a sulphonated ethylene-propylene-diene polymer. The modified organoclay is particularly suitable for use in low toxicity invert mud systems.

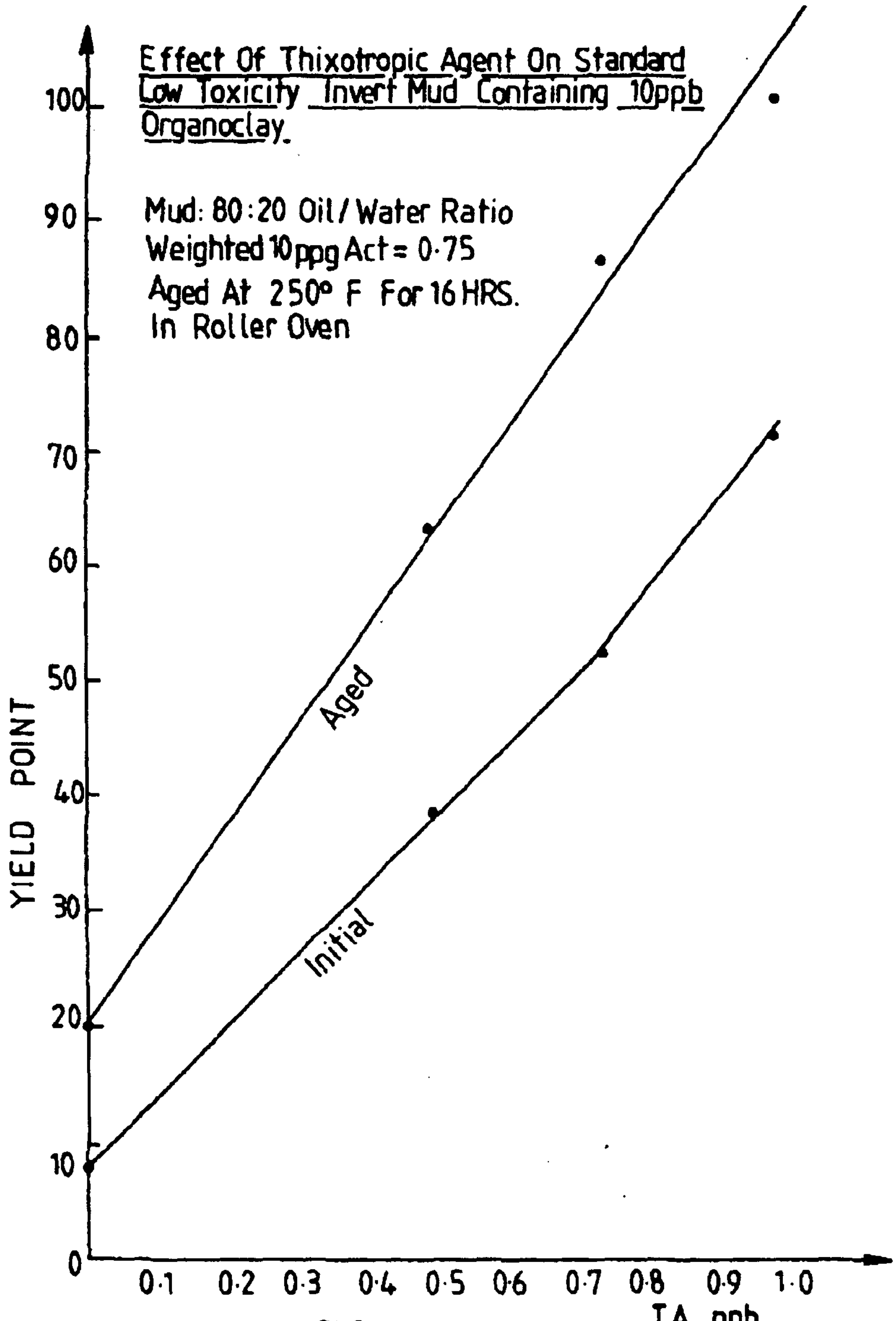
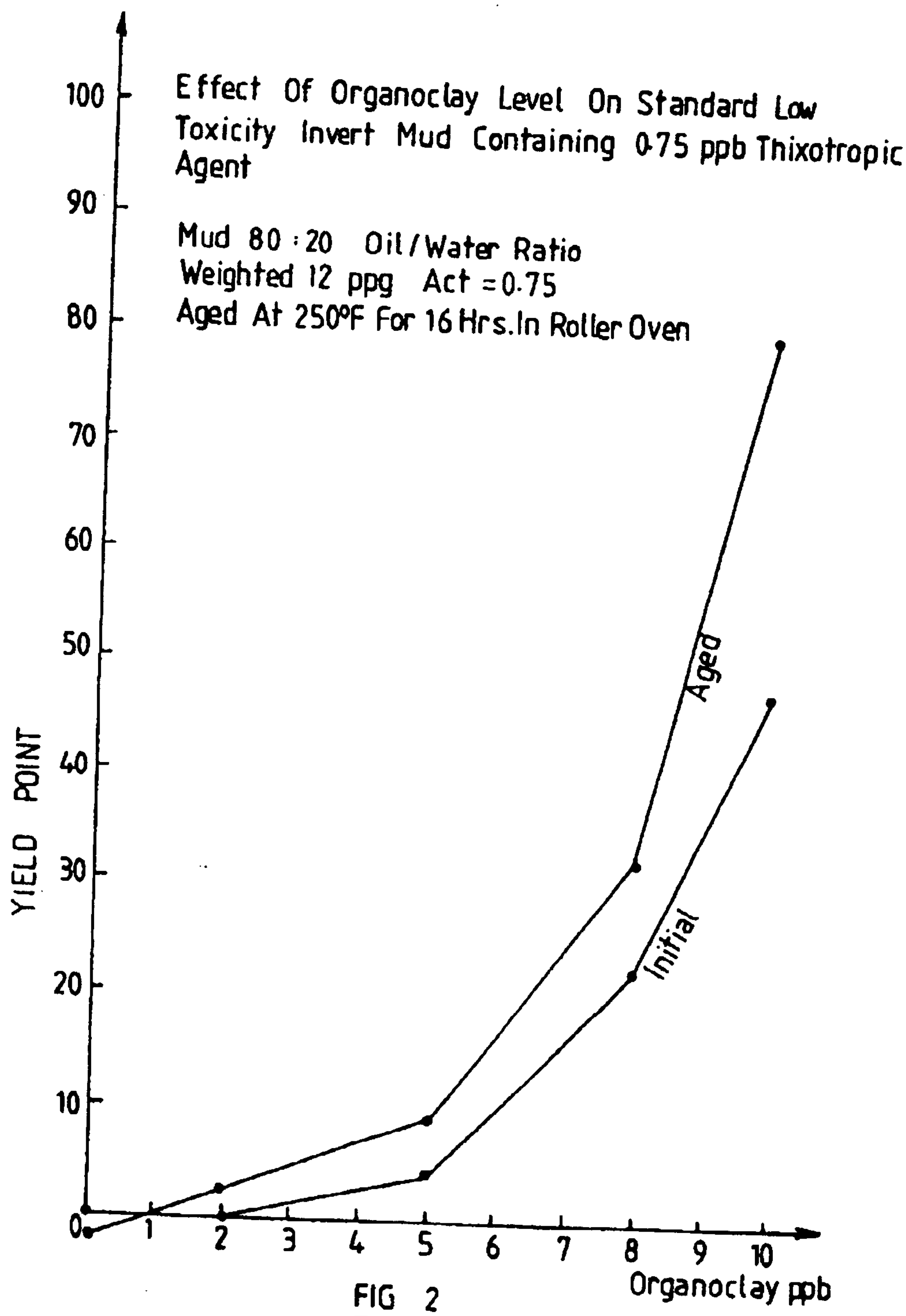

Effect Of Thixotropic Agent On Standard Low Toxicity Invert Mud Containing 10ppb Organoclay
Mud: 80:20 Oil/Water Ratio
Weighted 10ppg Act = 0·75
Aged At 250° F For 16 HRS.
In Roller Oven
YIELD POINT
100
90
80
70
60
50
40
30
20
10
0
Aged
Initial
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
TA ppb

FIG.1



Effect Of Organoclay Level On Standard Low Toxicity Invert Mud Containing 0·75 ppb Thixotropic Agent
Mud 80 : 20 Oil/Water Ratio
Weighted 12 ppg Act = 0·75
Aged At 250°F For 16 Hrs. In Roller Oven
YIELD POINT
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
Organoclay ppb
Aged
Initial

FIG 2

SPECIFICATION

Additives for controlling or modifying thixotropi properties

This invention relates to materials for use as additives for controlling or modifying thixotropic properties of systems such as drilling muds.

One commonly used type of such additive comprises organoclays, that is to say clays such as Bentonite and others which have been reacted with an amine, particularly a quaternary ammonium compound and especially such a compound containing long chain carbon radicals. Such organoclays are useful in practice but suffer from a number of disadvantages, including cost and availability of raw materials, the often limited applicability of specific organoclays for specific systems, and undesirable variation of the thixotropic properties of the system in use.

For example, the parameters known as "yield point" and "gell strength" are particularly significant respectively in relation to the shear thinning property and ability of the liquid to support the solid constituents of the system in suspension. It is well known that in organoclay-containing drilling mud systems the values of the yield point and gell strength change in use from initial values which apply to the system as initially prepared to aged values which apply to the system after a period of use. The initial values need to be sufficiently high to maintain solids in suspension, but since ageing normally increases the yield point, it should be not so high initially as to make the system excessively viscous when aged.

Attempts to provide new organoclays using different quaternary ammonium compounds have met with some success, but at the cost of requiring expensive starting materials which are not always readily available in commercial quantities.

Various alternatives to organoclays have also been proposed, most notably organic polymers of different kinds, but such materials also tend to be expensive to produce and are more likely to be unstable at higher temperatures so that their thixotropic properties may be impaired or destroyed when the system is in use.

The present invention arises from the surprising discovery that the addition of relatively small quantities of certain organic polymers to an organclay additive can markedly improve the thixotropic properties and performance of the organoclay especially in low toxicity invert mud systems, i.e. water-in-oil emulsions based on oils with a low aromatic content. In particular, it has been found possible in such systems to achieve an improved initial yield point at room temperature under low shear conditions without undue increase in aged yield point thereby facilitating the make-up of the formulation. Also, it appears likely that additives in accordance with the invention will be more widely applicable than organoclays used alone, in that they are less sensitive to other additives employed in the system in which they are used.

According to the invention we provide an an additive for use in controlling the rheological properties of a low toxicity invert drilling mud, comprising an amine-treated clay and a salt of an organic amine and a sulphonated ethylene-propylene diene polymer.

The proportion of the polymer salt may be of the order of 10% or less relative to the organoclay, and the degree of sulphonation of the polymer need only be relatively low, typically of the order of 20 m.mole/100g.

It should be noted that it has previously been proposed to employ sulphonated polymers themselves as viscosifiers for drilling muds, but at concentrations of several pounds per barrel (ppb), i.e. at levels comparable with those at which organoclays themselves are employed, with consequent increase in costs. However, the addition of a few percent of the polymer salt to an organoclay in accordance with the invention results in the usage of the polymer salt at extremely low levels, with consequent cost saving, whilst significantly improving the properties obtained compared with the use of the organoclay alone.

The invention also resides in the use of an organoclay material incorporating a minor proportion of a salt of an organic amine and a sulphonated ethylene-propylene diene terpolymer as an additive for controlling or modifying the thixotropic properties of a low toxicity invert drilling mud and such a mud incorporating such an additive.

The following examples will serve to illustrate the utility of mixtures of organoclays and sulphonated EPDM polymers as thixotropic agents, in low toxicity invert drilling mud systems.

EXAMPLE 1

In a series of tests designed to screen various polym ric materials for use in onjunction with organoclays to modify and improve the thixotropic properties of such organoclays, a wide range of polymeric materials was tested in conjunction with a commercial organoclay in a commercial low toxicity oil based drilling mud. Thes tests showed no improvement of the thixotropic properties with the addition of organic polymers such as methacrylates, carboxylated acrylic polymer, ethylen -acrylic acid copolymer, amides of polyacrylic acid, stry ne-maleic anhydride polym r, styrene-butadiene polym r and thylene-vinylacetate polymer, in that measur d values of th initial and aged yi ld point of syst ms incorporating such polymers did not differ signifi-

cantly from a comparabl system without any such polymer.

Likewise, the addition of an thylene propylen diene polymer (EPDM) provided littl improvement. However, the addition of a small proportion of a long chain amine salt of a sulphonated EPDM produced marked changes in the thixtropic properties of the system. Table 1 illustrates the results of preliminary tests in a system with and without an EPDM polymer, at varying levels of sulphonation and at varying clay/polymer ratios. The results show quite strikingly that the addition of approximately 5 to 10 percent (relative to the organoclay) of a sulphonated EPDM in the form of a long chain amine salt produces a marked increase in the initial yield point without undue effect on plastic viscosity, whilst the gell strength values are proportionately higher.

In these examples, the organic polymer used was a commercially available EPDM rubber having a Mooney viscosity in the range 35 to 45 which was sulphonated with acetyl sulphate generated in situ from acetic anydride and concentrated sulphuric acid. The EPDM rubber was dissolved in hexane with gentle warming. An excess of acetic anhydride was added, followed by concentrated sulphuric acid, accurately dispensed, with stirring. After half an hour at room temperature, aliquots of the sulphonic acid were taken and neutralised immediately with either sodium hydroxide (in the case of Example 1 9) or with a long chain secondary amine, specifically di-hydrogenated tallow amine (2HT). The polymeric salt was isolated from the solvent either by steam stripping or by isolated by precipitation with alcohol, followed by drying in an oven at 50°C and milling to form a powder. The same EPDM rubber was used in all examples except 1.8, which employed a higher molecular weight rubber.

As can be seen from Table 1, the effect on the rheological properties of the drilling mud system in which the additives are used varies according to the degree of sulphonation (Examples 1.3, 1.4 and 1.7) and with the ratio of sulphonated polymer to organoclay (Examples 1.4, 1.5 and 1.6). The results suggest that sulphonation to approximately 20 m.mole is optimum and that best results in the drilling mud system are obtained with the sulphonated polymer at a level of approximately 5% relative to the organoclay. The use of sodium hydroxide as a neturalising *agent established that the use of sodium as the cation for the polymer salt does not provide a* suitable product, and for use in a low toxicity (low aromatic) oil-based system, it is apparent that the cation must include at least one long chain carbon substituent to give the required solubility in an invert system.

EXAMPLE 2

For a further series of tests, a further batch of sulphonated EPDM rubber was produced as described above, to a theoretical sulphonation level of 22 m.mole/100g and the product was neutralised with 2HT.

Again, the amine salt was blended with a commercially available organoclay to produce mixes comprising 5% and 7% (by weight) of the amine salt. These mixes were then tested in a low toxicity oil mud system at a standard level of 10 ppb and compared with samples utilising the organoclay alone and the amine salt alone. The results are illustrated in Table 2.

These results confirm that an addition of approximately 5% of a long chain amine salt of a sulphonated EPDM polymer to a conventional organoclay produces a significant improvement in the initial yield point and gell strength without detriment to the plastic viscosity, whilst use of the polymer salt alone in similar quantities has no significant effect on the rheology of the system.

EXAMPLE 3

A further series of tests were conducted to show the effect of varying quantities of the amine salt of sulphonated EPDM produced as described above. The results are illustrated graphically in Fig. 1. In each case the stated quantity of salt was added to a standard low toxicity invert mud (80:20 oil/water ratio) containing 10 ppb organoclay.

EXAMPLE 4

Finally a series of tests were conducted to show the effect of varying quantities of organoclay. In each case the stated quantity of organoclay was added to a standard low toxicity invert mud (80:20 oil/water ratio) containing 0.75 ppb amine salt of sulphonated EPDM produced as described abov .

Further tests using different organoclays and differ nt oil based mud systems have produced similar results. It is also believed that similar r sults may be achi ved by th use of different polymers and other long chain sulphonated amines, possibly with adjustment of the degree of sulphonation to compensate for variations in the molecular weight of th polymer and the amine.

These r sults clearly illustrate th improvement which r sults from the incorporation of a relatively small proportion of a salt of a long chain amine and a sulphonat d EPDM polymer togeth r with conventional organoclays.

Instead of preparing the salt using EPDM rubber dissolved in hexane, oth r solvents may be

may be used in the form of solution in such high flash oil. Such a solution can be added to the mud formulation when the latter is made up, as a further ingredient in addition t the organoclay. Alternatively, such a solution can be added t the organoclay during processing of the latter so as to be deposited on the organoclay particularly by solvent evaporation or the dry powder can be blended with the organoclay during the manufacture of the latter.

Further it is contemplated that amines other than 2HT may be employed in the production of the salt, such as tallowamine (a primary amine), N-methyl di-hydrogenated tallowamine (a tertiary amine), and similar amines derived from alternative feedstocks such as cocoa, rape seed oil, etc.

TABLE I

Example No.	Organoclay ppb	EPDM ppb	SO_3^- m.mole	Neutralization Source	Plastic[1] Viscosity Init.	Plastic[1] Viscosity Aged	Yield[1] Point Init	Yield[1] Point Aged	Gell Strength[1] 10sec/10min Initial	Gell Strength[1] 10sec/10min Aged	Notes
1.1	10	nil	—	—	24	39	1	17	4/8	13/22	Control
1.2	9	1	nil	—	31	40	5	24	6/8	18/23	No SO_3^-
1.3	9	1	10	2HT	37	46	15	44	9/15	37/54	
1.4	9	1	22	2HT	36	46	35	72	18/26	54/63	
1.5	9.5	0.5	22	2HT	23	34	12	42	7/12	47/57	
1.6	9.8	0.2	22	2HT	22	34	6	32	6/8	28/34	
1.7	9	1	35	2HT	34	49	32	72	19/32	63/69	
1.8	9	1*	22	2HT	38	45	17	53	13/18	32/42	*higher mol. wt. incomplete solution
1.9	9	1	22	NaOH	-	-	-	-	-	-	Insoluble

(1) Values expressed in "Fann Units" derived from readings on a Fann viscometer.
All viscosities measured at 115°

TABLE 2

Example No.	Total Additive ppb	Organoclay %	Amine Salt %	Plastic Viscosity Init.	Plastic Viscosity Aged	Yield Point Init.	Yield Point Aged	Gell Strength 10sec/10min. Initial	Gell Strength 10sec/10min. Aged	Notes
2.1	10	100	nil	33	39	1	14	4/7	14/19	Control
2.2	10	93	7	39	59	57	79	28/40	77/86)	Mixtures
2.3	10	95	5	36	39	20	57	9/19	56/68)	
2.4	1	nil	100	19	19	-3	1	2/2	3/3)	Amine salt alone
2.5	2	nil	100	43	54	-3	3	4/5	7/9)	

CLAIMS

1. A low toxicity invert drilling mud which incorporates up to 20 ppb of an amine-treated clay and between 5% and 10% (by weight relative to said clay) of a salt of an organic amine and a sulphonated ethylene-propylene diene polymer.

2. A drilling mud according to Claim 1 wherein said amine is a long chain amine.

3. A drilling mud according to Claim 2 wherein said amine is a secondary amine.

4. A drilling mud according to Claim 1 wherein said amine is an hydrogenated tallow amine.

5. A drilling mud according to Claim 4 wherein said amine is a di-hydrogenated tallow amine.

6. An additive for use in controlling the rheological properties of a low toxicity invert drilling mud, comprising an amine-treated clay and a salt of a organic amine and a sulphonated ethylene-propylene diene polymer.

7. An additive according to Claim 6 wherein said amine is a long chain amine.

8. An additive according to Claim 7 wherein said amine is a secondary amine.

9. An additive according to Claim 6 wherein said amine is an hydrogenated tallow amine.

10. An additive according to Claim 9 wherein said amine is a di-hydrogenated tallow amine.

11. An additive according to Claim 6 and substantially as hereinbefore described in Example 1.

12. A drilling mud according to Claim 1 and substantially as hereinbefore described in Examples 1 to 4.

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